



Project Summary

Source Sampling Fine Particulate Matter: Wood-Fired Industrial Boiler

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Fine particulate matter of aerodynamic diameter 2.5 μm or less ($\text{PM}_{2.5}$) has been implicated in adverse health effects, and a National Ambient Air Quality Standard for $\text{PM}_{2.5}$ has been promulgated (July 1997) by the U. S. Environmental Protection Agency. A national network of ambient monitoring stations has been established to assist states in determining areas which do not meet the ambient standard for $\text{PM}_{2.5}$. For such areas, it is important to determine the major sources of the $\text{PM}_{2.5}$ so the states can devise and institute a control strategy to attain the ambient concentrations set by the standard.

A tool often used by states in apportioning ambient $\text{PM}_{2.5}$ to the sources is a source-receptor model. Such a model requires knowledge of the $\text{PM}_{2.5}$ chemical composition emitted from each major source contributing to the ambient $\text{PM}_{2.5}$ as well as the chemical composition of the $\text{PM}_{2.5}$ collected at the receptor (ambient monitoring) sites. The report provides such a profile for a wood-fired industrial boiler equipped with a multistage electrostatic precipitator (ESP) control device. Along with the $\text{PM}_{2.5}$ emission profile, data are also provided for gas-phase emissions of several organic compounds. Data are provided in a format suitable for inclusion in the EPA source profile database, SPECIATE.

This Project Summary was developed by the National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully

documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Source profiles for PM emissions to date have been limited mostly to PM of aerodynamic diameter of 10 μm or less (PM_{10}) and have consisted of only elemental composition data. For certain sources, where the emitted PM is carbonaceous in nature, a knowledge of the organic species present in the PM can greatly improve the utility of the profile for source apportionment purposes. Therefore, the principal objective of this study was to acquire such organic speciation data for an industrial wood-fired boiler in a form and of a quality suitable for use in source-receptor modeling.

The industrial boiler selected for testing was a relatively modern, watertube, pneumatic, vibrating stoker-type unit fueled with wood/bark chips via a continuous screw-feed conveyor belt. When operated at the design heat input rate, the boiler generated 74,843 kg/hr (165,000 lb/hr) of superheated steam, 65.3 atm/404 °C (960 psig/760 °F). Emissions were controlled by a multicyclone type dust collector followed by a multistage ESP.

Fuel, acquired from the local municipality, was derived principally from tree trimming waste that had passed through a chipper/shredder. This material was stored outdoors in a large pile until used so that the type, age, and moisture content of the wood fuel fed to the boiler varied from day to day. Sampling was conducted over a 2-day period in August 2000.

Experimental Methods

To relate source emissions measurements to ambient pollutant concentrations, it is important that the measurement techniques used to characterize and quantify source emissions are consistent with the techniques used for ambient pollutant measurements. A source sampling strategy to eliminate many potential biases between source and ambient sampling measurements is to use the same sampling and analytical techniques for both source and ambient monitoring. Therefore, for this study, a source sampler was used which diluted the hot exhaust emissions (ca. 50:1 dilution) with cleaned ambient air to near ambient temperature and pressure prior to collection of the source samples. Additionally, emissions were provided a sufficient residence time at near-ambient conditions prior to sample collection such that semivolatile compounds in the diluted exhaust could distribute between the gas and particle phases as they would in the ambient environment.

The custom-built dilution sampler followed the basic design originated by L.M. Hildemann et al., but was modified to allow for continuous automatic adjustment of exhaust and dilution air flow rates and for ease in assembly and transportation. Dilution air was ambient air which had passed through a high-efficiency particulate air (HEPA) filter, an activated carbon bed, and a final Teflon® membrane filter before mixing with the exhaust gas. Integrated samples of the cleaned dilution air were also collected during the course of a test run, and exhaust samples were corrected for any contaminants which may have remained in the dilution air after cleaning.

Particulate samples were collected for organic analyses using two different types of sampling arrays. One array consisted of a cyclone with a d_{50} cut point of 2.5 μm , followed by a series of two 200 mm long annular denuders coated with XAD-4 resin, followed by a quartz fiber filter, followed by two polyurethane foam (PUF) plugs. The other array was the same but without the annular denuders. The purpose of the annular denuders was to remove gas-phase semi-volatile organic compounds (SVOCs) prior to the quartz filter so as to avoid a positive adsorption artifact on the quartz filter sample. Quartz filters were prebaked at 550 °C for 12 hr, and annular denuders and PUF plugs were solvent-cleaned prior to use to remove organic contaminants prior to sampling. Teflon membrane filters were used to collect $\text{PM}_{2.5}$ samples for mass, inorganic ion, and elemental measurements.

Two dinitrophenylhydrazine (DNPH)-coated silica gel cartridges in series were used to collect volatile carbonyl compounds. An electropolished stainless steel canister was used to collect gas-phase samples for analysis of volatile organic compounds (VOCs) and selected air toxic compounds.

The organic and elemental carbon content of the quartz filter $\text{PM}_{2.5}$ samples was determined by the National Institute of Safety and Health (NIOSH) Method 5040 using a Sunset Laboratory thermal optical transmittance instrument. Individual organic compounds present in the $\text{PM}_{2.5}$ samples collected on the quartz filters were determined by extracting the filters with hexane and a 2:1 mixture by volume of benzene and isopropanol. Prior to extraction, the filters were composited as necessary to achieve a total of approximately 0.5 mg of organic carbon and were spiked with a mixture of deuterated internal recovery standards.

An aliquot of the combined organic extract was derivatized with diazomethane to yield methyl esters of any fatty acids. An aliquot of the methylated extract was further derivatized with bis(trimethylsilyl) trifluoroacetamide-N,O-bis(trimethylsilyl)acetamide to convert compounds such as levoglucosan and cholesterol to their trimethylsilyl derivatives. Both derivatizations were performed in order to allow these compounds to be separated and eluted from a gas chromatography column. Gas chromatography/mass spectrometry was used to identify and quantify the individual organic compounds present in the extracts. Target compounds were positively identified by comparing mass spectra of the analytes with those obtained for over 100 authentic compound standards.

The organic compounds were quantitated by referencing each compound to one or more deuterated internal standards spiked into the sample to correct for losses of the analytes which may have occurred in the compositing, extracting, concentrating, and derivatizing steps. An extensive set of standards of target compounds at known concentrations, which also included the deuterated internal standard compounds, was used to establish 3- or 5-point calibration curves from which the concentrations of the analytes were determined.

PM mass was determined gravimetrically by weighing the Teflon filters before and after sample collection. These filters were maintained at 20-23 °C and a relative humidity of 30-40% for a minimum of 24 hr prior to weighing on a microbalance. Elemental analysis was carried out

by x-ray fluorescence spectrometry. Water soluble ions were analyzed by ion chromatography.

Carbonyl compounds collected on the DNPH-coated cartridges were analyzed using EPA Compendium Method TO-11a. Air toxics and speciated nonmethane organic compounds were determined according to the procedures of EPA Compendium Method TO-15 and an EPA technical assistance method, respectively.

Results

Total speciated nonmethane organic compound mass emission rates were 13.19 and 3.45 mg/kg fuel for sampling days 1 and 2, respectively. Total VOC (speciated plus non-speciated) mass emission rates were 22.64 and 6.49 mg/kg fuel on sampling days 1 and 2, respectively. Emission rates of total gas-phase carbonyl compounds ranged from 8.27 (day 1) to 2.90 mg/kg fuel (day 2). Average $\text{PM}_{2.5}$ mass emission rates were 3.54 and 1.23 mg/kg fuel for sampling days 1 and 2, respectively.

An explanation for the observed difference in mass emission rates of both gaseous and $\text{PM}_{2.5}$ emissions between the 2 test days could not be deduced with confidence. Both the boiler and sampling system operating parameters were essentially identical for both days. The only apparent variable which may have contributed to the difference in emission rates was the nature of the chipped wood fuel itself since the fuel was selected from different locations in the large on-site storage pile during the 2 days of testing. However, only one composited wood fuel sample from the storage pile was analyzed, so any significant difference in boiler feed between the two tests could not be determined.

Concentrations of propylene, methylene chloride, and benzene in the diluted exhaust gas were higher than typically found in ambient air. However, the concentrations of propylene and methylene chloride in the diluted exhaust gas were about the same as found in the cleaned dilution air, indicating that these two compounds were present in both ambient air and in the source emissions at about the same level. Benzene concentrations in the diluted exhaust gas were nearly 3 orders of magnitude higher than concentrations observed in the dilution air, indicating that this compound was emitted from the source at relatively high levels compared to ambient levels.

Elemental carbon and organic carbon content of the $\text{PM}_{2.5}$ collected on quartz filters was found to be highly dependent on whether an XAD-coated denuder was

inserted in the sampling line prior to the filter. Without the denuder, the amount of organic carbon found on the quartz filters was 2.6 times the amount found with the denuder, thus providing confirmatory evidence for a positive adsorption artifact on the quartz filters when no denuder was present.

Of the major water soluble ions, only sulfate and potassium ions were above quantitation limits. Total potassium as measured by x-ray fluorescence spectrometry agreed well with water-soluble potassium determined by ion chromatography. Silicon was the element found in greatest concentration in the PM_{2.5}, perhaps originating from the fire-brick lining of the boiler.

Individual organic compounds comprising the organic carbon fraction of the PM_{2.5} emissions consisted mostly of polynuclear aromatic hydrocarbons (PAHs), alkanes (>C15), alkanolic acids (>C8), and the iso- and anteiso-alkanes. Levoglucosan, a marker compound for biomass combustion, was found in the particulate matter but not in the relatively large amounts characteristic of open burning of biomass material or emissions from wood-fired domestic appliances. Resin acids (e.g., pimaric, isopimaric, and sandarapimaric acids) used as markers for softwood combustion and methoxyphenols used as markers for hardwood combustion also were not found above quantification limits. Therefore, the organic

compound emission profile for the wood-fired industrial boiler was very unlike profiles for residential woodstoves and fireplaces and for biomass open burning. This observation is not unexpected since the combustion regime for the boiler was substantially different from that of woodstoves and open burning and since the boiler emissions were controlled by an ESP whereas wood burning appliances and open burning are typically uncontrolled.

A complete compilation of the over 300 gas- and particle-phase speciated compounds is available in tabular form in the full report in a format suitable for inclusion in the EPA SPECIATE emission profile database.

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N. Dean Smith is the EPA Project Officer (see below).

The complete report, entitled "Source Sampling Fine Particulate Matter: Wood-Fired Industrial Boiler," will be available at <http://www.epa.gov/ORD/NRMRL/Pubs> or as Order No. PB2002-105739 (Cost: \$44.00, subject to change) from:

National Technical Information Service
5285 Port Royal Road
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